



Assessment of high (diurnal) to low (seasonal) frequency variations of isoprene emission rates using a neural network approach

C. Boissard, F. Chervier, A. L. Dutot

► To cite this version:

C. Boissard, F. Chervier, A. L. Dutot. Assessment of high (diurnal) to low (seasonal) frequency variations of isoprene emission rates using a neural network approach. Atmospheric Chemistry and Physics, 2008, 8 (7), pp.2101. hal-00328578

HAL Id: hal-00328578

<https://hal.science/hal-00328578>

Submitted on 10 Oct 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Assessment of high (diurnal) to low (seasonal) frequency variations of isoprene emission rates using a neural network approach

C. Boissard, F. Chervier, and A. L. Dutot

Laboratoire Interuniversitaire des Systèmes Atmosphériques, Universités Paris 12 et Paris 7, CNRS, 61 avenue du Général de Gaulle, 94010 Créteil Cedex, France

Received: 27 July 2007 – Published in Atmos. Chem. Phys. Discuss.: 22 August 2007

Revised: 20 February 2008 – Accepted: 26 March 2008 – Published: 11 April 2008

Abstract. Using a statistical approach based on artificial neural networks, an emission algorithm (ISO-LF) accounting for high to low frequency variations was developed for isoprene emission rates. ISO-LF was optimised using a data base (ISO-DB) specifically designed for this work, which consists of 1321 emission rates collected in the literature and 34 environmental variables, measured or assessed using National Climatic Data Center or National Centers for Environmental Predictions meteorological databases. ISO-DB covers a large variety of emitters (25 species) and environmental conditions (10° S to 60° N). When only instantaneous environmental regressors (instantaneous air temperature T_0 and photosynthetic photon flux density L_0) were used, a maximum of 60% of the overall isoprene variability was assessed with the highest emissions being strongly underestimated. ISO-LF includes a total of 9 high (instantaneous) to low (up to 3 weeks) frequency regressors and accounts for up to 91% of the isoprene emission variability, whatever the emission range, species or climate investigated. ISO-LF was found to be mainly sensitive to air temperature cumulated over 3 weeks (T_{21}) and to L_0 and T_0 variations. T_{21} , T_0 and L_0 only accounts for 76% of the overall variability.

biogenic or BVOC, are key species in atmospheric chemistry processes. Indeed, global biogenic volatile organic compound fluxes are believed to exceed their anthropogenic inputs by a factor of 10 (Müller, 1992; Guenther et al., 1995) and, due to their high reactivity, they were shown, on regional to global scale, to significantly influence atmospheric chemistry and climate (Fehsenfeld et al., 1992; Simpson, 1995; Poisson et al., 2000; Steinbrecher et al., 2000; Sanderson et al., 2003). Therefore, the assessment of accurate and highly resolved BVOC emission fluxes represents a major goal for environmental issues and in particular of isoprene (C_5H_8) fluxes, the major BVOC (Guenther et al., 1995; Simpson et al., 1999).

However, due, in part, to a variability which ranging over several orders of emission magnitude, isoprene emission assessments remain critical and uncertain. Those variations are resulting from a complex set of biophysical regulations to ambient condition changes. Indeed, isoprene emission variability is closely triggered by leaf developmental stage and emissions occur only when leaves are grown or are growing. For deciduous trees, induction of isoprene emissions was observed to happen 200, 300, and 400 cumulated degree day (d.d., °C) after bud break for *Quercus macrocarpa* (Petron et al., 2001), *Quercus alba* (Geron et al., 2000) and *Populus tremuloides* (Monson et al., 1994) respectively. Highest emissions are generally observed for fully developed leaves. For *Quercus alba* and *Quercus Macrocarpa* maximal isoprene emissions were observed 600 and 700 d.d. respectively after bud break. Depending on local environmental conditions, such d.d. values were reached within a period of time ranging from few days to 3 weeks. With leaf senescence, isoprene emissions decrease down to non detectable levels. Moreover, when a leaf is emitting, the rapid enzymatic activity adaptations can lead to an additional type of fast (seconds to minutes) variations of isoprene emissions. Such “instantaneous” variations are well described by specific emission algorithms based on instantaneous photosynthetic photon flux

1 Introduction

Chemistry-Transport models are commonly used to assess, at local or global scales, the distribution of tropospheric species, such as ozone. Appropriate and accurate emission data are needed to initialise their chemical modules. Emissions of gaseous compounds in the atmosphere can be related to human activities and natural processes. Volatile organic compounds emitted from vegetation, usually referred to as



Correspondence to: C. Boissard
(boissard@lisa.univ-paris12.fr)

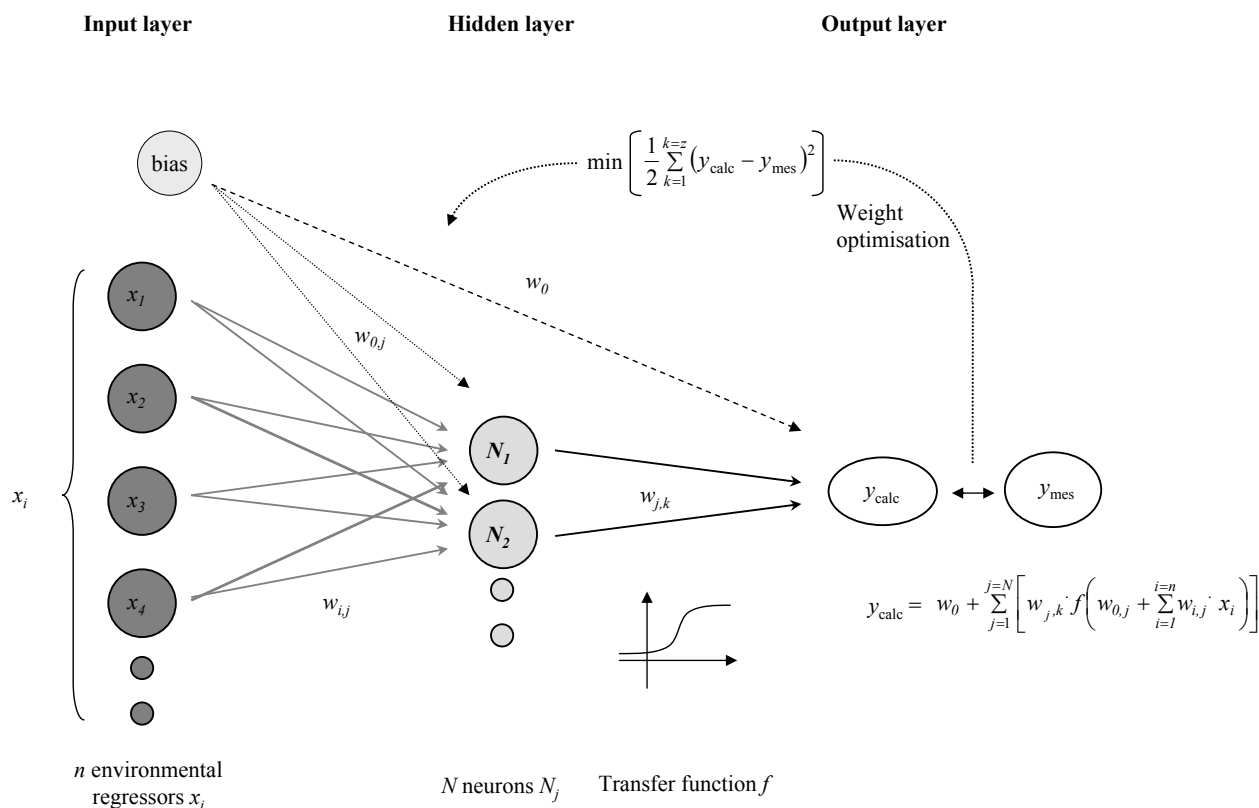


Fig. 1. Structure and principle of a Multi Layer Perceptron. Output values y_{calc} are assessed by a weighted sum of input parameters x_i . w_0 is the connecting weight between the bias (initial random values optimised to obtain the co-ordinate at the origin of the neuronal regression) and y_{calc} , $w_{j,k}$ the connecting weight between the neuron N_j and y_{calc} , $w_{0,j}$ the connecting weight between the bias and the neuron N_j , and $w_{i,j}$ the connecting weight between the input x_i and the neuron N_j .

density (PPFD) and air temperature (G93 algorithm, Guenther et al., 1993), or on the previous day PPFD and air temperature values (Lehning et al., 1999; Zimmer et al., 2000; Fischbach et al., 2002). Another source of emission variations, in some occasions even more critical than leaf developmental stage, originates from the acclimation of a plant to more or less long term environmental changes. For instance, the onset of kudzu isoprene emissions were observed to be shortened by one week under elevated temperature growth conditions compared to cold growth conditions (Wiberley et al., 2005). Light acclimation was found to be more complex for oak species, with a first impact observed within few hours and a second one after 4–6 days (Hanson and Sharkey, 2001). Similarly, isoprene emissions from mature oak leaves were found to be significantly correlated with air temperatures averaged over the previous first, 2 and 7 days (T_1 , T_2 and T_7 respectively) and with photosynthetic active radiations averaged over the previous 2 days (PPFD2), the strongest correlation being with $T_2 \times \text{PPFD2}$ (Sharkey et al., 1999).

Most of the general parameterisations developed so far for isoprene emissions (e.g. Tingey et al., 1979; Guenther et al., 1991; Guenther et al., 1993; Sharkey and Loreto, 1993;

Lehning et al., 2001; Guenther et al., 2006; Arneth et al., 2007) assign an emission factor to an emitter or a group of emitters which is then modulated by some relevant environmental parameters (air temperature, light intensity and CO_2) prevailing over a period ranging from few minutes to 10 days before the measurement. However, these parameterisations mainly describe the most rapid variations of isoprene emissions and do not consider acclimation over more than 10 days (Guenther et al., 2006). Nevertheless, lower frequency (e.g. seasonal) variations of a tree capacity to release isoprene were observed to account for a significant, in some cases the major, part of the overall observed emission fluctuations, and reach up to 3 orders of standardised emission rates magnitude (Monson et al., 1994; Geron et al., 2000; Boissard et al., 2001; Petron et al., 2001). If not correctly assessed this low frequency variability can represent a major source of discrepancies in isoprene emission assessments (Guenther et al., 1995).

Artificial neural networks (ANNs) have shown in various occasions their capacity to account for some complex sets of environmental interactions. For instance, multiple non-linear regression technique based on ANNs was employed

by Lasseron (2001) to assess variations of *Ulex europaeus* isoprene emission rates using environmental parameters integrated over few days to few weeks prior to the measurements. Simon et al. (2005) used a similar technique to couple isoprene and monoterpene emissions measured from Amazonian tree species with physiological and environmental regressors. ANNs were also used to provide kilometer scale emission maps of European forest carbon fluxes (Papale and Valentini, 2003), and to improve assessments of biogenic soil NO_x emission variations (Delon et al., 2007).

In this study, using an appropriate database specifically built for this work (ISO-DB), ANNs were implemented in order to develop an isoprene emission rate algorithm (ISO-LF) accounting for high (instantaneous) to low (weeks) frequency variations of ambient conditions and for a large set of species. ISO-LF development, performances and sensitivity are presented and discussed.

2 Method

2.1 The overall strategy

A similar methodology than the one employed by Lasseron (2001) for *Ulex europaeus* was used for this work but applied to a wider range of isoprene emitters and environmental conditions. Briefly, non linear regressions between isoprene emission rates reported in the literature and a set of environmental parameters were calculated and examined. Physiological parameters, such as net assimilation, transpiration, stomatal conductance were not considered due to their difficulty to be assessed afterward when not directly provided in the literature reference. Moreover, when both, environmental and physiological input parameters, were considered, best assessments of isoprene and monoterpene emissions were found, in tropical conditions, to be obtained when environmental information (instantaneous PPFD and air temperature, and averaged temperature of the preceding 48–18 h) was employed (Simon et al., 2005).

Non linear regressions were assessed using ANNs. Among the other available statistical methods, ANNs present the advantage of being the most parsimonious (Dreyfus et al., 2002). Moreover, ANN approach, as the other non-linear regression methods, is not, or not very, sensitive to regressor co-linearity (Bishop, 1995; Dreyfus et al., 2002).

2.2 Neural network description and setting

The neural network developed in this study was used as a Multi Layer Perceptron (MLP). Further details concerning the MLP theory can be found in Aleksander and Morton (1990) and White (1992). Briefly, a MLP consists in a network of processing units (the neurons or artificial neurons) N_j , all connected to each other and arranged in different layers (input, hidden and output layer, Fig. 1). Such a

neuron arrangement learns (or approximates) during a training phase the information contained in a set of experimental data or output data y_{mes} (in our case the isoprene emission rates). When the MLP is trained, a set of n inputs data x_i (in our case, the environmental parameters) is processed several times in order to adjust a weighted sum $x_i \cdot w_{i,j}$ where $w_{i,j}$ represents the optimised weights calculated by non-linear regressions to y_{mes} . $x_i \cdot w_{i,j}$ is then modified (or transferred) by a transfer function f in order to calculate y_{calc} as follows:

$$y_{\text{calc}} = w_0 + \sum_{j=1}^{j=N} \left[w_{j,k} \cdot f \left(w_{0,j} + \sum_{i=1}^{i=n} w_{i,j} \cdot x_i \right) \right] \quad (1)$$

where w_0 is the connecting weight between the bias (initial random values optimised to obtain the co-ordinate at the origin of the neuronal regression) and y_{calc} , N the number of neurons N_j , $w_{j,k}$ the connecting weight between the neuron N_j and y_{calc} , $w_{0,j}$ the connecting weight between the bias and the neuron N_j , and $w_{i,j}$ the connecting weight between the input x_i and the neuron N_j . The transfer function f consists of a parameterised asymptotic “S” shape function such as sigmoid or hyperbolic tangent. The training process starts from randomised values of weights which are iteratively adjusted using a second order Quasi Newton back propagation technique until the minimum difference E between y_{mes} and y_{calc} reaches the point where the first derivative of E equals zero. For this study, E was calculated as follows:

$$E = \frac{1}{2} \sum_{k=1}^{k=z} (y_{\text{calc}} - y_{\text{mes}})^2 \quad (2)$$

where z is the number of output values. For our study, a large number (300) of iterations were selected for every ANN run in order to make sure that E did not correspond to a local error minimum. During a validation phase, or blind validation, ANN performances are assessed by the root mean square error RMSE obtained for these data which were not used during the training phase. A special set of validation data is thus required before start.

The training/validation data splitting represents a key step in the neural approach. For this work, the training-validation division was first carried out by considering different climates (tropical, temperate with dry summer, temperate without dry summer, and cold and humid). For every climate, data were then classified according to their emission strength (strong, medium and small as in Guenther et al., 1995). Each of the 11 sub datasets thus obtained was finally splitted between training (80%) and validation (20%) data using a Kullback-Leibler distance function (Kullback, 1951) to insure a statistical homogeneity. The final training ($n=1062$) and validation ($n=259$) databases consist of the union of each training and validation sub-datasets. As shown in Fig. 2, both databases were statistically homogeneous, with training mean, first, second, and third quartile values of 30.01,

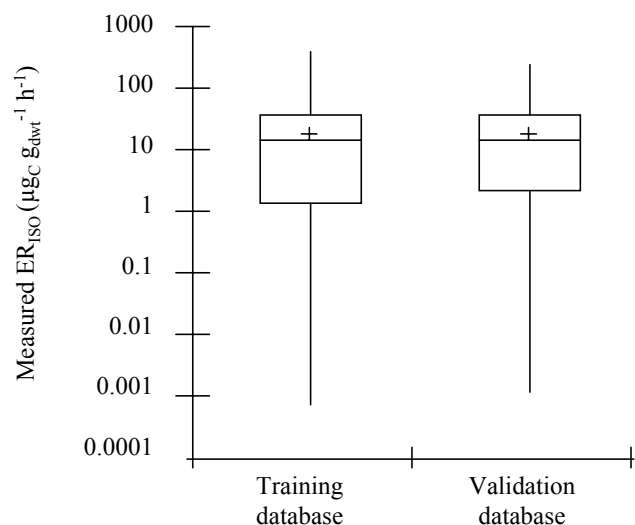


Fig. 2. Comparison of the statistical characteristics of ISO-DB isoprene emission rates for the training ($n=1065$) and validation ($n=259$) databases. The lower, medium and upper horizontal bars correspond to the first, median and 3rd quartile respectively. Mean values are represented by crosses. Minimum and maximum values are represented by the vertical bars.

1.87, 14.57 and $38.53 \mu\text{gC (g foliar dry weight)}^{-1} \text{h}^{-1}$ (hereafter, $\mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$) respectively, close to the validation values of 30.39, 2.75, 16.08 and $38.50 \mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$ respectively. The highest ($3.3 \times 10^2 \mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$) and smallest ($5.0 \times 10^{-4} \mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$) isoprene emission rates were forced into the training database, since the neural approach is only valid within interpolation.

The neural network developed in this study was based on a commercial version of the Netral NeuroOne software (v. 6.0–<http://www.netral.com>, France)

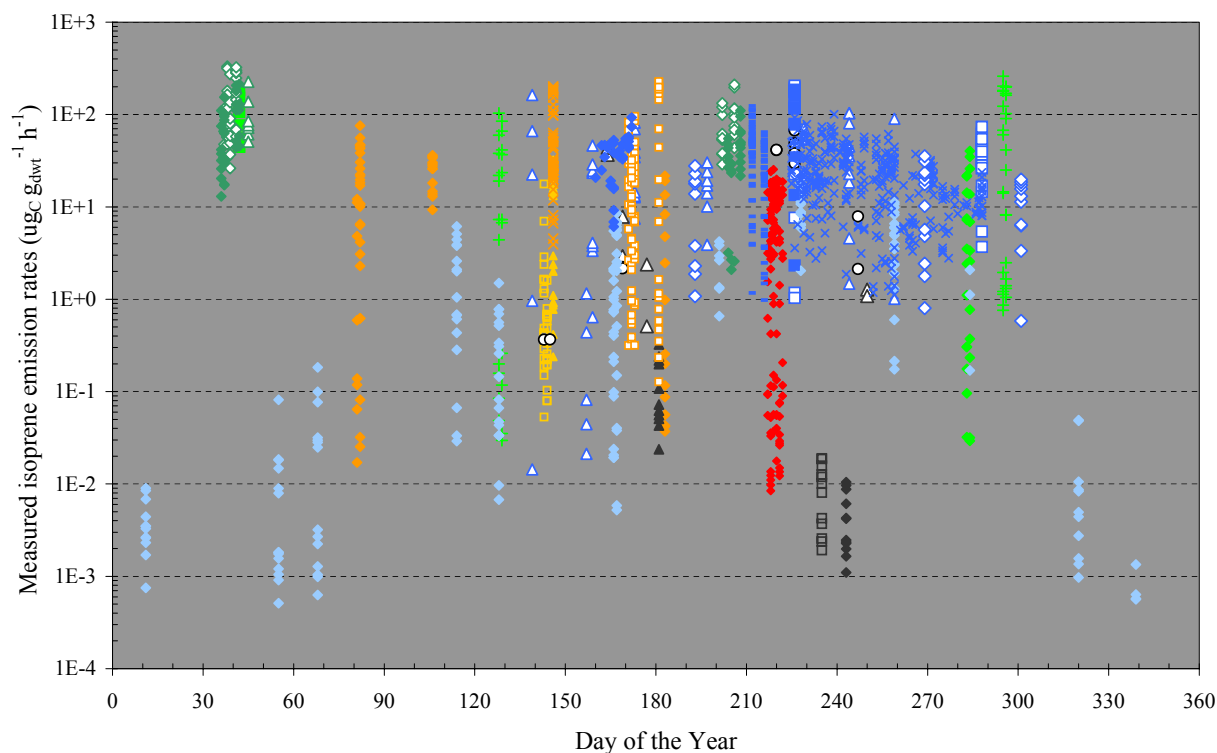
2.3 ISO-DB description

The isoprene database ISO-DB designed for this study consists of:

1. isoprene emission rate values ($n=1321$) extracted in the literature and obtained from previous in-situ studies. Most of the data collected were available under figures which were digitally numerised. All emission rates were expressed in ISO-DB in $\mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$. Leaf based emission rates were considered and converted into mass based emission rates only when a specific leaf mass conversion factor was provided together with the data. Isoprene emissions being negligible at night, only daytime data were used. All emission rates represent branch level measurements carried out at the top of the canopy, except for *Liquidambar* whom emission rates were additionally measured 12 m under the top of the 22 m canopy. Most (93%) of the measurements were

obtained using branch enclosure technique, the other 7% from leaf cuvette system. A total of 25 broadleaved and coniferous trees species, grown under environmental conditions ranging from tropical (10°S) to boreal (60°N) climates were considered (Table 1). Most of these species are representative of moderate to high isoprene emitters (i.e. standardised emissions rates higher than 35 and $70 \mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$ respectively, as in Guenther et al., 1995). Emission rate values were shown to vary over more than 4 orders of magnitude, from, approximately, 5×10^{-4} to $3 \times 10^2 \mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$ (Fig. 3), with a mean and median value of 30.1 and $14.8 \mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$ respectively.

2. the temperature (T_0) and PPFD (L_0) values, hereafter referred to as “instantaneous”, recorded during the sampling time; T_0 and L_0 values were found to range from 2 to 42°C (0 to $2400 \mu\text{mol m}^{-2} \text{s}^{-1}$ respectively), with a mean and median value of 25.1 and 25.5°C (680 and $590 \mu\text{mol m}^{-2} \text{s}^{-1}$ respectively).
3. 32 other environmental regressors which were examined for their ability to account for environmental changes during and before the emission measurements (Table 2). They were integrated over 1 to 21 days preceding the measurements using daily mean values extracted from NCDC meteorological data for air temperatures and rainfall or NCEP reanalysis data for soil variables and solar radiations. All the selected meteorological stations were within a 30 km distance of each measurement site, except for the Kuhn et al. (2002, 2004) data obtained in Brazil for which data from a meteorological station located within 200 km were used. Similarly, environmental data were missing in 1984 at the Nagoya station for Ohta (1986) *Quercus serrata* measurements. Meteorological data available in 1984 at the nearest station Shionomisaki located approximately at 200 km was corrected by the differences obtained between both stations over the 1994–2004 decade. Canopy effects on light and temperature were accounted for *Liquidambar* shaded leaves according to the Lamb et al. (1993) model. The daylight length D_1 , considered for its capacity in discriminating the seasonal period of measurement, was calculated as:



Climate type	Tree type		
	CEV	BLD	BLEG
C		△ <i>Populus tremula</i>	
		○ <i>Salix philiciforia</i>	
T	▲ <i>Pseudotsuga menziesii</i>	◆ <i>Liquidambar</i> (shaded)	◆ <i>Ulex europaeus</i>
	◆ <i>Thuja plicata</i>	■ <i>Pendula loud</i>	
	■ <i>Tsuga mertensiana</i>	□ <i>Platanus orientalis</i>	
		△ <i>Populus balsamifera</i>	
		— <i>Quercus alba</i>	
		× <i>Quercus rubra</i>	
Td	◆ <i>Abies borisii</i>	◆ <i>Eucalyptus globulus</i>	□ <i>Erica arborea</i>
		× <i>Quercus frainetto</i>	▲ <i>Myrtus communis</i>
		□ <i>Quercus pubescens</i>	
		■ <i>Astronium graveolens</i>	◆ <i>Ficus insipida</i>
TR		+ <i>Hymenea courbaril</i>	
		◆ <i>Luehea semanii</i>	
		◆ <i>Sorocea guilleminiana</i>	
		△ <i>Spondias mombin</i>	

Fig. 3. Measured isoprene emission rates ($\mu\text{gC g}_{\text{dwt}}^{-1} \text{h}^{-1}$) compiled in ISO-DB vs the day of year of their measurement, according to the tree type (coniferous evergreen, CEV; broadleaved deciduous, BLD; and broadleaved evergreen, BLEG) and to the climate (cold, C; temperate, T; temperate with dry summer, Td, and tropical, TR).

Table 1. Isoprene emission rates computed in ISO-DB. Species type: broadleaved deciduous (BLD), broadleaved evergreen (BLEG), and conifer evergreen (CEV). Is(G95): standardised isoprene emission rates as assigned in Guenther et al. (1995). Climate types: tropical (TR), cold (C), temperate without dry season (T), and temperate with dry summer (Td). The range of emission rate ER values is given, together with their mean (figure in parenthesis) in $\mu\text{gC g}_{\text{leaf}}^{-1} \text{h}^{-1}$. * Original data (isoprene emission rates, instantaneous air temperature and photosynthetic photon flux density) were numerised from figure (F) and/or are raw data given by the authors (RD). (1) Boissard et al., 2001; (2) Drewitt et al., 1998; (3) Hakola et al., 1998; (4) Hansen et al., 1997; (5) Harley et al., 1997; (6) Harrison et al., 2001; (7) Keller and Lerdau 1999; (8) Kesselmeier (personnel communication); (9) Kuhn et al., 2002; (10) Kuhn et al., 2004; (11) Nunes and Pio, 2001; (12) Ohta 1986; (13) Pier 1995; (14) Simon et al., 1998; (15) Steinbrecher et al., 1997; (16) Xiaoshan et al., 2000. ISO-DB data are available at <http://www.lisa.univ-paris12.fr/~boissard>.

Emitter	Is (G95)	Measurement information										References
		Lat.	Lon.	Location	Date	Day of the Year	Climate type	n	ER	Canopy position	Data*	
Abies Borisii-regis	CEV	16	39.54	21.44° E	Pertouli, GRC	08/1997	Td	105	0.01–25.55	(6.66)	F+RD	(6)
Astronium graveolens	BLD	24	9.1	79.6° W	Panama city, PAN	02/1997	TR	7	44.72–183.34	(94.53)	F	(7)
Erica arborea	BLEG	16	41.6	12.5° E	Castelporziano, ITA	05/1994	Td	36	0.05–17.67	(1.37)	F+RD	(4)
Eucalyptus globulus	BLD	45	40.4	8° W	Tabua, PRT	03/1994	Td	33	0.02–75.85	(17.67)	F	(11)
Ficus insipida	BLEG	24	9.1	79.6° W	Panama city, PAN	02, 07/1997	TR	56	26.13–331.34	(119.16)	F	(7)
Hymenaea courbaril	BLD	24	–10.08	62.54° W	Rondônia, BRA	05/1999	TR	51	0.03–260.44	(55.92)	F+RD	(9) (10)
Liquidambar styraciflua	BLD	45	33.8	84.33° W	NE d'Atlanta, USA	06/1993	Td	32	6.12–92.64	(38.69)	F+RD	(5)
Luehea seemanii	BLD	24	9.1	79.6° W	Panama city, PAN	07/1996	TR	59	2.09–214.49	(62.9)	F	(7)
Myrtus communis	BLEG	16	41.6	12.5° E	Castelporziano, ITA	05/1994	Td	20	0.24–32.24	(11.69)	F+RD	(4)
Pendula loid	BLD	45	40	116.4° E	Pékin, CHN	08/1998	T	10	2.31–189.48	(96.56)	F	(16)
Platanus orientalis	BLD	45	40	116.4° E	Pékin, CHN	10/1998	T	37	1.03–205.38	(58.38)	F	(16)
Populus balsamifera	BLD	45	49.1	122.8° W	Lower Fraser	09/1995	T	34	0.01–162.49	(31.26)	F	(2)
Populus tremula	BLD	45	60.4	25° E	Valley (LFV), CAN	09/1996	C	8	0.51–43.70	(12.02)	T	(3)
Pseudotsuga menziesii	CEV	8	49.1	122.8° W	Nord d'Helsinki, FIN	06/1995	T	11	0.02–0.32	(0.12)	F	(2)
Quercus alba	BLD	45	35.57	84.17° W	Oak ridge, USA	07, 08/1992	T	91	0.98–123.79	(36.58)	F + RD	(5)
Quercus frainetto	BLD	45	41.6	12.5° E	Castelporziano, ITA	05/1994	Td	47	3.93–202.26	(63.34)	F	(15)
Quercus pubescens	BLD	45	43.45	3.45° E	Viols en Laval, FRA	06/1995	Td	100	0.12–227.49	(35.21)	F+RD	(8) (14)
Quercus rubra	BLD	45	34.51	87.18° W	Rogersville, USA	10/1992	T	302	0.58–35.33	(13.11)	F+RD	(13)
Quercus serrata	BLD	45	35.2	136.9° E	Nagoya, JPN	10 / 1984	T	32	0.36–67.14	(23.42)	F	(12)
Salix phylicifolia	BLD	45	60.4	25° E	Nord d'Helsinki, FIN	05, 06, 08/1996	C	12	0.36–67.14	(23.42)	T	(3)
Soroea guilleminiana	BLD	24	–10.08	62.54° W	Rondônia, BRA	10/1999	TR	25	0.03–40.38	(8.36)	F+RD	(10)
Spondias mombin	BLD	24	9.1	79.6° W	Panama city, PAN	02/1997	TR	7	5086–225.42	(101.18)	F	(7)
Thuja plicata	CEV	8	49.1	122.8° W	LFV, CAN	08/1995	T	12	0.001–0.01	(0.005)	F	(2)
Tsuga mertensiana	CEV	8	49.1	122.8° W	LFV, CAN	08/1995	T	12	0.001–0.02	(0.01)	F	(2)
Ulex europaeus	BLEG	5	54.2	2.6° W	Wray, GBR	09/1994 to 09/1995	T	140	0.001–18.12	(2.76)	F+RD	(1)
						11, 55, 68, 114, 128, 201, 228, 259						
			52.8	1.5° E	Kelling Heath, GBR	06 / 1995		42				

$$D1 = \frac{24}{\pi} \arccos(-\tan \lambda \tan(\arcsin(\sin \delta \cdot \cos[\frac{2\pi}{n}(r-172)]))) \quad (3)$$

where λ is the latitude, $\delta=23.45^\circ$ the Earth inclination, r the day of the year, and n the annual number of days.

2.4 Data pre-processing

Values of each input were compiled in ISO-DB using a same unit (Table 2). Because each input is expressed in a different unit, absolute values are highly variable from one input to another. To prevent any input regressor x_i to get an artificially stronger weight in the neural regressions, every input was centrally-normalised as follows:

$$x_{i(CN)} = \frac{x_i - \bar{x}_i}{s_{x_i}} \quad (4)$$

where \bar{x}_i is the x_i mean and s_{x_i} its associated standard deviation, both calculated over the entire database. Isoprene emission rates were similarly treated. In addition, due their large range of variation (5 orders of emission magnitude), log values were used in the ANNs.

3 Results and discussion

When not mentioned, results hereafter presented were obtained for validation data.

3.1 Are $L0$, $T0$, $L1$ and $T1$ sufficient to account for the overall BVOC emission variability?

In order to make sure that the variability of ISO-DB emissions is not only triggered by high frequency environmental changes, the impacts of $L0$, $T0$, $L1$ and $T1$, recognised for their role in describing short term acclimation of isoprene emissions (Guenther et al., 1993; Geron et al., 2000; Lehnig et al., 2001) were evaluated. Two series of ANN tests were conducted: with $L0$ and $T0$ only (ANN0 case) and with $T0$, $T1$, $L0$ and $L1$ (ANN01 case). ANN0 accounted for a maximum of 60% of the isoprene emission variability (Table 3). When $L1$ and $T1$ were additionally considered in the ANNs, 10% of the isoprene variability could additionally be accounted for, which represents, at the 95% confidence level, a significant improvement compared to ANN0 case. Most of the remaining 30% of the variability not described was associated with the highest isoprene emissions which were underestimated by up to two orders of magnitude (results not shown), whatever the species or the environmental conditions.

3.2 ISO-LF development

The development of ISO-LF was carried out by training the ANNs until the best combination between a relevant set of environmental regressors x_i and a network structure

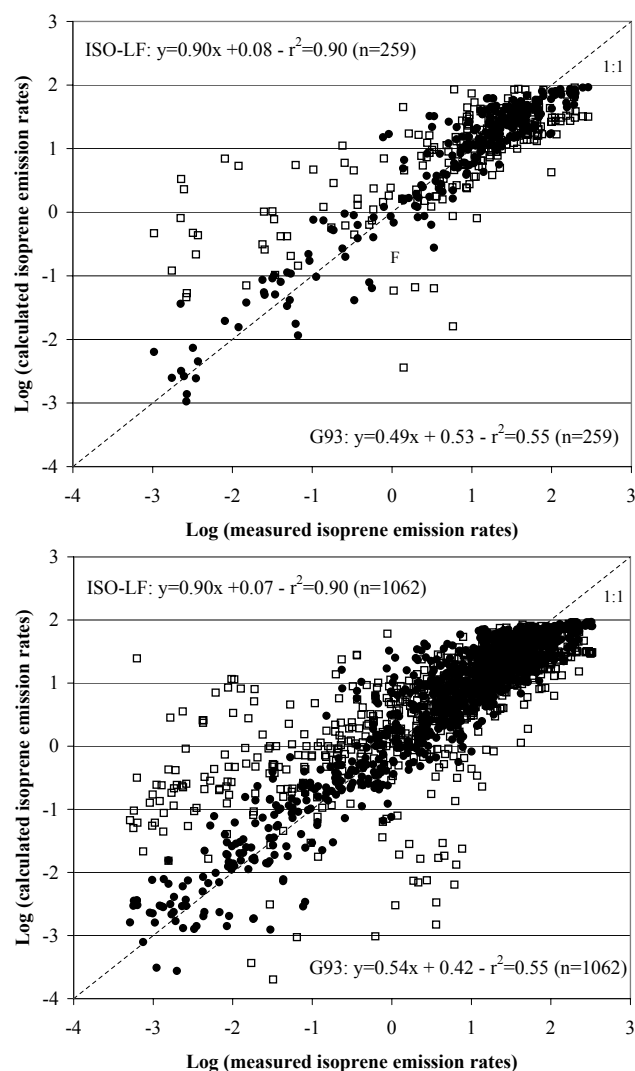


Fig. 4. Comparison between the log of isoprene emission rates calculated using ISO-LF (black circles) and G93 (open squares, Guenther et al., 1993, with $I_s=5 \mu\text{gC g}_{\text{dw}}^{-1} \text{h}^{-1}$) vs. the measured isoprene emission rates for (a) validation data and (b) training data. The 1:1 line is shown (dotted line).

(i.e. number of neurons and of neuron layers, transfer function, number of iterations) was obtained. Further details of the neural training can be found in Dutot et al. (2007).

In term of neuronal structure, the number of iterations was fixed at 300 and a second order Quasi-Newton back-propagation employed. Among the different transfer functions available, the hyperbolic tangent tanh was used. A number of 1 to 7 neurones were tested. $\text{RMSE}_{\text{validation}}$ was shown to decrease for a higher number of neurons until a minimum value of 0.293 was reached for $N=4$. When more than 4 neurons were used, $\text{RMSE}_{\text{validation}}$ was showed to increase again indicating an overtraining phenomenon (data not shown).

Table 2. Tested ISO-DB environmental input regressors assessed using daily mean values, except for $T0$ and $L0$ (instantaneous). Daylight length $D1$ is in h, air and soil temperatures in $^{\circ}\text{C}$, $L0$ in $\mu\text{mol m}^{-2} \text{s}^{-1}$, solar fluxes $L1$ – $L21$ in W m^{-2} , precipitations in mm and soil water contents in fraction of volume (0–1). * are regressors rejected using the variable probe technique and the covariance analysis. $^{\circ}$ are regressors showing a weak influence on the overall isoprene variability. In bold, the regressors eventually considered in ISO-LF.

Environmental information			x_i not cumulated			x_i cumulated over p days preceeding the d-day (included)			
			Instantaneous	(d-1) day mean	(d-1) day mean	p			
						2	6	13	20
Daylight duration			$D1^{\circ}$						
Air	Temperature	mean	$T0$	$T1$			$T7^{\circ}$	$T14^*$	$T21$
		maximum			$T1m^*$				
		minimum			$T1m$				
	Light intensity		$L0$	$L1$			$L7^{\circ}$	$L14^{\circ}$	$L21^*$
	Precipitations			$P1^*$		$P3^*$	$P7^*$	$P14$	$P21$
Soil	Upper layer (0–10 cm)	Temperature			$ST1u$		$ST7u^{\circ}$	$ST14u^*$	$ST21u^{\circ}$
		Water content			$W1u^*$		$W7u^*$	$W14u^{\circ}$	$W21u^{\circ}$
	Deep layer (10–200 cm)	Temperature			$ST1d^*$		$ST7d^*$	$ST14d^*$	$ST21d^*$
		Water content			$W1d^*$		$W7d^*$	$W14d^{\circ}$	$W21d^{\circ}$

Table 3. Comparison of the performances (slope s , correlation coefficient r^2 , root mean square error RMSE and mean bias error MBE) obtained using ($L0$, $T0$) – ANN0 case, ($L0$, $T0$, $L1$, $T1$) – ANN01 case, ($L0$, $T0$, $T21$) – ANN021 case, ($L0$, $T0$, $L1$, $T1$, $T21$) – ANN0121 case, and ISO-LF.

	ANN0	ANN01	ANN021	ANN0121	ISO-LF
s	0.567	0.683	0.739	0.82	0.898
r^2	0.564	0.695	0.763	0.846	0.901
RMSE	0.775	0.649	0.486	0.383	0.293
MBE	−0.014	−0.035	−0.011	−0.004	−0.002

Using the statistical probe technique (Chen et al., 1989) and a covariance analysis, 15 of the 34 inputs x_i were rejected since they were found to have no statistical influence on isoprene emissions (Table 2). For every of the 19 remaining x_i , the slope of $y_{\text{calc}} = f[(x_i) \bar{x}]$ (where \bar{x} is the mean for every input x_j , $j=i-1$ and $j \neq i$) was examined. For 10 of them, a slope close to zero was obtained, indicating their weak influence on the overall isoprene variability. They were no longer considered in the ANN trainings, and, as shown in Table 2, a total of 9 x_i were eventually considered in ISO-LF: the instantaneous air temperature $T0$ and light intensity $L0$, the (d-1) day mean ($T1$) and minimum ($T1m$) air tem-

peratures, solar radiation ($L1$) and soil temperatures ($ST1u$), the precipitation cumulated over 14 and 21 days ($P14$ and $P21$ respectively), and the air temperature cumulated over 21 days $T21$. When a single one of these 9 inputs was excluded from the statistical analysis, isoprene emission assessment error was, at the 95% confidence level, significantly increased. One third of ISO-LF inputs represents adaptations on a time scale of at least one week, and more than half of them ($T0$, $L0$, $L1$, $T1m$ and $T21$) was previously reported as positively influencing isoprene emissions under in-situ conditions.

The general equation obtained for ISO-LF is given in appendix A.

3.3 ISO-LF performances

As shown Fig. 4a and b, ISO-LF was found to account for 90% of the overall isoprene emission variability, a result which is, at the 95% confidence level, significantly better than for the G93 algorithm (55%, Fig. 4a,b), and the ANN0 (56%) or ANN01 cases (70%) (Table 3). Moreover, this good performance was obtained over the whole emission range, including the highest emission values, and whatever the climate or the species type. The few outliers correspond to statistically poorly represented situations (e.g., for some of the *Ulex europaeus* measurements, sudden cloud

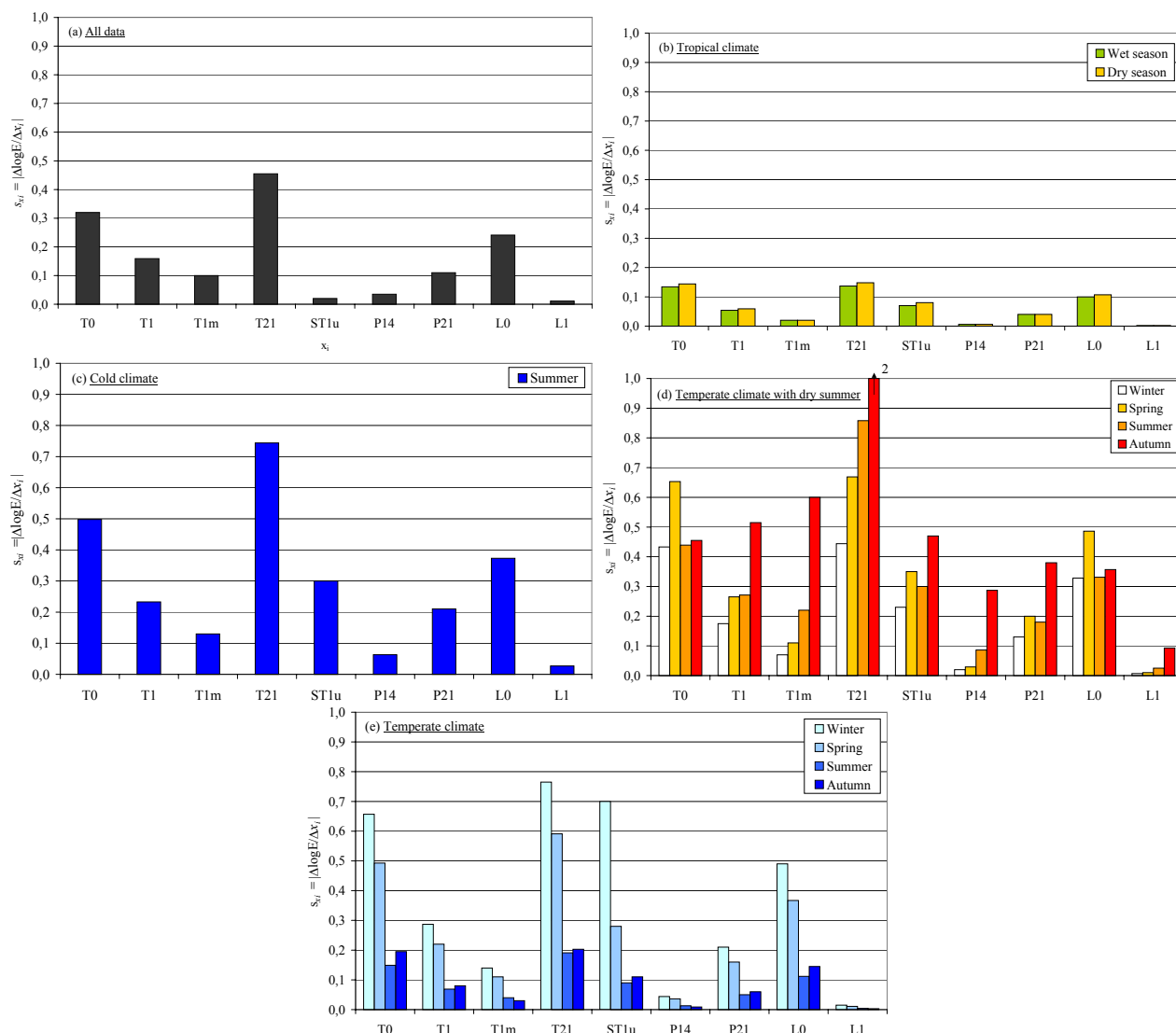


Fig. 5. ISO-LF sensitivity (s_{xi}) to the inputs x_i , for (a) all ISO-DB data, (b) tropical climate date (wet and dry season), (c) cold climate data (summer only), (d) temperate climate with dry summer (all seasons), and (e) temperate climate (all seasons). s_{xi} was calculated by varying x_i , while all the other inputs x_j ($j=i-1$ and $j \neq i$) were fixed to their mean values.

occurrences during sampling or summer late afternoon samplings with low light intensity but still elevated temperature). As shown in Table 3, the air temperature cumulated over several weeks (T_{21}), previously observed to account for some of the seasonal variations of isoprene emissions (Monson et al., 1994; Geron et al., 2000), was found, at the 95% confidence level, to significantly improve the results obtained for ANN0 and ANN01 cases: 76 and 85% of isoprene variability was accounted for in the ANN021(T_0 , L_0 , T_{21}) and ANN0121(T_0 , L_0 , T_1 , L_1 , T_{21}) case respectively. However, ISO-LF performances were, at the 95% confidence level, found to remain better ($r^2=0.90$) and, in particular, for the highest and lowest emission rates which were poorly assessed in the ANN021 and ANN0121 (data not shown).

3.4 ISO-LF sensitivity

When non linear regressions are used, the weight of each individual factor in the global variance, (here, the sensitivity of isoprene emission rates variability to every of the $9x_i$ used in ISO-LF) is rather complex to assess and the interpretation of the results not straightforward. However, in order to help in having an idea to which environmental variable x_i ISO-LF is more sensitive, s_{xi} was calculated as follows:

$$s_{xi} = \left| \left(\frac{\Delta \log y_{calc}}{\Delta x_i} \right)_{\bar{x}_j} \right| \quad (5)$$

where Δy_{calc} is the variation of the predicted isoprene emission rate obtained for a given variation Δx_i of the input x_i , while the other inputs were set to their mean \bar{x}_j , where $j=i-1$ and $j \neq i$. s_{xi} was calculated (i) for the entire dataset and (ii) for data related to 4 different climates (temperate with and without dry summer, tropical, and cold and humid) and for every season (only summer for cold climate).

As shown in Fig. 5a, ISO-LF is, on the overall, mainly sensitive to $T21$ ($s_{T21}=0.46$), and to $T0$ ($s_{T0}=0.32$) and $L0$ ($s_{L0}=0.25$), whatever the climate or the season. $T1$, $T1m$ and $P21$ were found to have a smaller weight on the predicted isoprene emission variability ($s_{xi} < 0.2$) and the lowest sensitivity of ISO-LF was observed for $ST1u$ and $L1$ (s_{xi} of 0.02 and 0.04 respectively).

s_{xi} values appeared to be correlated with the magnitude of the environmental condition fluctuations (Fig. 5b–e): the lowest s_{xi} were generally associated with data measured under tropical climate ($s_{xi} < 0.15$, Fig. 5b), when higher s_{xi} values were obtained for more contrasted climates. The overall s_{xi} pattern of every climate remains, however, similar to the one obtained with all data, except for $P14$ in autumn for temperate climate with dry summer data (Fig. 5d), and for $ST1u$ (the upper layer soil temperature of the preceding day) which represents the second most important contributor in winter under temperate climate (Fig. 5e). Soil nutrient uptake, such as nitrogen, is known to be strongly dependent on the micro-organism activity, which is itself directly controlled by soil temperature (e.g. Bassirirad, 2000). However, direct impacts of soil temperature on isoprene emissions having not been reported so far, the observed $ST1u$ predominance remains unclear. Moreover, this result cannot be generalised due to the poor statistical representation of winter conditions under temperate climate which relies only on *Ulex europaeus* measurements. Under temperate climate with dry summer, isoprene emission regulation was found to be critically dependent on autumnal conditions, with most of the highest s_{xi} obtained for this season (Fig. 5d). Unexpected high monoterpene emissions have been previously measured in several occasions in the Mediterranean area in October (Bertin et al., 1997; Owen et al., 1998). This observation and our finding suggest that BVOC emissions from plant growing within Mediterranean climates may be quite sensitive to autumnal conditions, in particular to low frequency variations of air temperature ($S_{T21} > 2$). For temperate climate data, $T21$ remains the dominant ISO-LF input (Fig. 5e), in particular during winter and spring (S_{T21} of 0.76 and 0.59 respectively).

4 Conclusions

Multiple non-linear regressions based on ANNs were implemented to develop an isoprene emission algorithm (ISO-LF) accounting for high (instantaneous) to low (weeks) frequency variations. 1321 isoprene emissions rates extracted from the literature were specifically compiled in a database (ISO-DB),

which covers a large variety of isoprene emitters (25 deciduous and coniferous species) grown under latitudes ranging from 10° S to 60° N, and describes a set of 34 environmental high to low frequency environmental regressors. The instantaneous air temperature $T0$ and light intensity $L0$ alone were found to account for a maximum of 60% of ISO-DB isoprene emission variability. When the preceding day information was additionally considered, this figure increases up to 70%, the remaining 30% being mostly associated with the highest emission rates.

ISO-LF algorithm, obtained from a best combination made of the (d-1) day minimum air and soil temperatures, the precipitations cumulated over 2 and 3 weeks, and the cumulated air temperature over 21 days ($T21$), accounts for up to 90% of the overall isoprene variability. None of these inputs were artificially selected in any of the ANN optimisation processes. ISO-LF was found to be mainly sensitive to $T0$, $L0$ and $T21$. More precisely, $T21$ was found to be particularly critical during spring for temperate climates, and during autumn for temperate climates with dry summers.

These findings are in agreement with previous experimental findings and prove the ability of ANNs to help in accounting for the complex regulations of BVOC emissions. This work also confirms that some parameters other than $L0$ and $T0$ can be successively considered to significantly reduce the uncertainties on isoprene emission assessments and that, among the different parameters, environmental ones represent a relatively straightforward solution.

ISO-LF can be routinely updated and improved by adding new emission data in ISO-DB. In particular, factors not available for this study (e.g. the nitrogen content or the soil characteristics known to affect the plant water and nutriment uptake) or broadly assessed with meteorological datasets should be tested and better assessed during ad-hoc seasonal campaigns (measurement of isoprene emissions and environmental information before and between samplings).

Such an approach could also be extended for other BVOC emissions such as monoterpenes or sesquiterpenes. BVOC canopy fluxes, rather than emission rates, would also be good candidates for such a neuronal approach.

Appendix A

Calculation of isoprene emission rates $E[\text{ISO-LF}]$ ($\mu\text{gC g}_{\text{dw}}^{-1} \text{h}^{-1}$) using the ISO-LF algorithm

$E[\text{ISO-LF}] = 10^{\log E[\text{ISO-LF}]}$ where $\log E[\text{ISO-LF}] = \log E[\text{ISO-LF}_{(CN)}] * s + m$ and s is the standard deviation of $\log(\text{ISO-DB})$ isoprene emission rates (1.2122), m is the mean of $\log(\text{ISO-DB})$ isoprene emission rates (0.7553), $\log E[\text{ISO-LF}_{(CN)}]$ the central-normalised \log_{10} of isoprene emission rates calculated as $\log[E[\text{ISO-LF}_{(CN)}]] = w_0 + w_{1,k}$.

Table A1. w : the optimised weights as follows:

w_0	−3.08618				
$w_{0,1}$	−0.89846	$w_{0,2}$	9.06389	$w_{0,3}$	4.87766
$w_{1,1}$	−0.27948	$w_{1,2}$	0.02752	$w_{1,3}$	−0.01802
$w_{2,1}$	−0.20780	$w_{2,2}$	0.15894	$w_{2,3}$	2.73633
$w_{3,1}$	−0.11346	$w_{3,2}$	4.78860	$w_{3,3}$	−0.19168
$w_{4,1}$	0.04658	$w_{4,2}$	−8.04591	$w_{4,3}$	−0.88332
$w_{5,1}$	−0.28604	$w_{5,2}$	14.91701	$w_{5,3}$	0.50996
$w_{6,1}$	−0.01218	$w_{6,2}$	2.27811	$w_{6,3}$	0.32972
$w_{7,1}$	0.08509	$w_{7,2}$	−0.13261	$w_{7,3}$	0.09713
$w_{8,1}$	0.15142	$w_{8,2}$	−2.52531	$w_{8,3}$	0.03432
$w_{9,1}$	−0.00431	$w_{9,2}$	0.11231	$w_{9,3}$	0.11136
$w_{1,k}$	−2.35616	$w_{2,k}$	−2.66701	$w_{3,k}$	1.71583
				$w_{4,k}$	2.71897

Table A2. x_i : the selected input regressors as follows:

x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9
T_0	L_0	T_{1m}	T_{1min}	T_{21}	P_{14}	P_{21}	$STlu$	L_1

$$\tanh(N_1) + w_{2,k} \cdot \tanh(N_2) + w_{3,k} \cdot \tanh(N_3) + w_{4,k} \cdot \tanh(N_4)$$

$$\text{where: } N_1 = w_{0,1} + \sum_{i=1}^{i=9} \sum_{j=1}^{j=9} w_{i,1} \cdot x_j$$

$$N_2 = w_{0,2} + \sum_{i=11}^{i=19} \sum_{j=1}^{j=9} w_{i,2} \cdot x_j$$

$$N_3 = w_{0,3} + \sum_{i=21}^{i=29} \sum_{j=1}^{j=9} w_{i,3} \cdot x_j$$

$$N_4 = w_{0,4} + \sum_{i=31}^{i=39} \sum_{j=1}^{j=9} w_{i,4} \cdot x_j$$

Acknowledgements. The authors wish to thank the French Research Ministry for funding F. Chervier's thesis work. We strongly acknowledge authors who kindly provided some raw information from their published data or complementary unpublished data, in particular J. Kesselmeier, (MPI Mainz, Germany) for *Quercus ilex* data.

Edited by: J. Williams

References

- Aleksander, I. and Morton, H.: An introduction to Neural Computing, Chapman and Hall, London, 1990.
- Arneth, A., Niinemets, Ü., Pressley, S., Bäck, J., Harri, P., Karl, T., Noe, S., Prentice, I. C., Serca, D., Hickler, T., Wolf, A., and Smith, B.: Process-based estimates of terrestrial ecosystem isoprene emissions: incorporating the effects of a direct CO₂-

isoprene interaction, *Atmospheric Chemistry and Physics*, 7, 31–53, <http://www.atmos-chem-phys.net/7/31/2007/>, 2007.

- Bassirirad, H.: Kinetics of nutrient uptake by roots: responses to global change, *New Phytol.*, 147, 155–169, 2000.
- Bertin, N., Staudt, M., Hanse, U., Seufert, G., Ciccioli, P., Foster, P., Fugit, J.-L., and Torres, L.: Diurnal and seasonal course of monoterpene emissions from *Quercus ilex* (L.) under natural conditions -Applications of light and temperature algorithms, *Atmos. Environ.*, 31, 135–144, 1997.
- Bishop, C. M.: Neural networks for pattern recognition, 504 pp., Oxford University Press, 1995.
- Boissard, C., Cao, X.-L., Juan, C.-Y., Hewitt, C. N., and Gallagher, M.: Seasonal variations in VOC emission rates from gorse (*Ulex europaeus*), *Atmos. Environ.*, 35, 917–927, 2001.
- Chen, S., Billings, S. A., and Luo, W.: Orthogonal least squares methods and their application to non-linear system identification. *International Journal of Control*, 50, 1873–1896, 1989.
- Delon, C., Serça, D., Boissard, C., Dupont, R., Dutot, A., Laville, P., De Rosnay, P., and Delmas, R.: Soil NO emissions modelling using artificial neural network, *Tellus*, 59B, 502–513, 2007.
- Drewitt, G. B., Current, K., Steyn, D. G., Gillespie, T. J., and Niki, H.: Measurement of biogenic hydrocarbon emissions from vegetation in the lower Fraser Valley, British Columbia, *Atmos. Environ.*, 32, 3457–3466, 1998.
- Dreyfus, G., Martinez, J.-M., Samuelides, M., and Thiria, S.: Réseaux de neurones: Méthodologie et applications, 386 pp., Eyrolles, 2002.
- Dutot, A.-L., Rynkiewicz, J., Steiner, F. E., and Rude, J.: A 24-h forecast of ozone peaks and exceedance levels using neural classifiers and weather predictors, *Env. modelling and software*, 22, 1261–1269, 2007.
- Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compounds, from vegetation and the implications for atmospheric chemistry, *Global Biogeochem. Cyc.*, 96, 389–430, 1992.
- Fischbach, R. J., Staudt, M., Zimmer, I., Rambal, S., and Schnitzler, J.-P.: Seasonal pattern of monoterpene synthase activities in leaves of the evergreen tree *Quercus ilex*, *Physiol. Plant.*, 114, 354–360, 2002.
- Geron, C. D., Guenther, A., Sharkey, T., and Arnts, R. R: Temporal

- variability in basal isoprene emission factor, *Tree Physiol.* 20, 799–805, 2000.
- Guenther, A., Zimmerman, P. R., and Fall, R.: Isoprene and monoterpene emission rate variability observations with eucalyptus and emission rate algorithm development, *J. Geophys. Res.*, 96, 10 799–10 808, 1991.
- Guenther, A. B., Zimmerman, P. R., and Harley, P. C.: Isoprene and monoterpene emission rate variability : model evaluations and sensitivity analysis, *J. Geophys. Res.*, 98, 12 609–12 617, 1993.
- Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., MacKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P. R.: A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, 100, 8873–8892, 1995.
- Guenther, A. B., Karl, T., Harley, P. C., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. and Phys.*, 6, 3181–3210, <http://www.atmos-chem-phys.net/6/3181/2006/>, 2006.
- Hakola, H., Rinne, J., and Laurila, T.: The hydrocarbon emission rates of tea-leaved willow (*Salix phylicifolia*), silver birch (*Betula pendula*) and European aspen (*Populus tremula*), *Atmos. Environ.*, 32, 1825–1833, 1998.
- Hansen, U., Van Eijk, J., Bertin, N., Staudt, M., Kotzias, D., Seufert, G., Fugit, J.-L., Torres, L., Cecinato, A., Brancaleoni, E., Ciccioli, P., and Bomboi, T.: Biogenic emissions and CO₂ gas exchange investigated on four Mediterranean shrubs, *Atmos. Environ.*, 31 SI, 157–166, 1997.
- Hanson, D. T. and Sharkey, T.: Effect of growth conditions on isoprene emission and other thermotolerance-enhancing compounds, *Plant Cell Environ.*, 24, 929–936, 2001.
- Harley, P. C., Guenther, A. B., and Zimmerman, P. R.: Environmental controls over isoprene emission in deciduous oak, *Tree Physiol.*, 17, 705–714, 1997.
- Harrison, D., Hunter, M. C., Lewis, A. C., Seakins, P. W., Nunes, T. V., and Pio, C. A.: Isoprene and monoterpene emission from the coniferous species *Abies Borisii-regis* – implications for regional air chemistry in Greece, *Atmos. Environ.*, 35, 4687–4698, 2001.
- Keller, M. and Lerdau, M.: Isoprene emission from tropical forest canopy leaves, *Global Biogeochem. Cyc.*, 13, 19–29, 1999.
- Kuhn, U., Rottenberg, S., Biesenthal, T., Wolf, A., Schbeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, M., and Kesselmeier, J.: Isoprene and monoterpene emissions of Amazonian tree species during the wet season: direct and indirect investigations on controlling environmental functions, *J. Geophys. Res.*, 107, 8071, doi:10.1029/2001JD000978, 2002.
- Kuhn, U., Rottenberg, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, M., and Kesselmeier, J.: Seasonal differences in isoprene and light-dependent monoterpene emission by Amazonian tree species, *Glob. Change Biol.*, 10, 1–20, 2004.
- Kullback, S.: On information and sufficiency, *Annals of mathematical statistics*, 22, 79–86, 1951.
- Lamb, B., Westberg, H., Gay, D., and Pierce, T.: A biogenic hydrocarbon emission inventory for the USA using a simple canopy model, *Atmos. Environ.*, 27, 1673–1690, 1993.
- Lasseron, L.: Modélisation des variations basse fréquence des émissions d'isoprène à l'aide d'un réseau de neurones artificiels, D.E.A. report, pp. 30, Paris 7 University, 2001.
- Lehning, A., Zimmer, I., Steinbrecher, R., Brüggeman, N., and Schnitzler, J.-P.: Isoprene synthase activity and its relation to isoprene emission in *Quercus robur* L. leaves, *Plant Cell Env.*, 22, 494–505, 1999.
- Lehning, A., Zimmer, W., Zimmer, I., and Schnitzler, J.-P.: Modeling of annual variations of oak (*Quercus robur* L.) isoprene synthase activity to predict isoprene emission rates, *J. Geophys. Res.*, 106, 3157–3166, 2001.
- Monson, R. K., Harley, P. C., Litvak, M. E., Wildermuth, M., Guenther, A. B., Zimmerman, P. R., and Fall R.: Environmental and developmental controls over the seasonal pattern of isoprene emissions from aspen leaves, *Oecologia*, 99, 260–270, 1994.
- Müller, J.-F.: Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases, *J. Geophys. Res.*, 97, 3787–3804, 1992.
- Nunes, T. V., and Pio, C. A.: Emission of volatile organic compounds from Portuguese eucalyptus forests, *Chemosphere-Global Change Science*, 3, 239–248, 2001.
- Ohta, K.: Diurnal and seasonal variations in isoprene emission from live oak, *Geochem. J.*, 19, 269–274, 1986.
- Owen, S., Boissard, C., Hagenlocher, B., and Hewitt, C. N.: Field studies of isoprene emissions from vegetation in the Northwest Mediterranean region, *J. Geophys. Res.*, 103, 25 499–25 511, 1998.
- Papale, D. and Valentini, R.: A new assessment of European forests carbon exchanges by eddy fluxes and artificial neural network spatialization, *Glob. Change Biol.*, 9, 525–535, 2003.
- Petron, G., Harley, P. C., Greenberg, J., and Guenther, A. B.: Seasonal temperature variations influence isoprene emission, *Geophys. Res. Lett.*, 28, 1707–1710, 2001.
- Pier, P. A.: Isoprene emission rates from northern red oak using a whole-tree chamber, *Atmos. Environ.*, 29, 1347–1353, 1995.
- Poisson, N., Kanakidou, M., and Crutzen, P. J.: Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere, *J. Atmos. Chem.*, 36, 157–230, 2000.
- Sanderson, M. G., Jones, C. D., Collins, W. J., Johnson, C. E., and Derwent, R. G.: Effects of climate change on isoprene emissions and surface ozone levels, *Geophys. Res. Lett.*, 30, 1936, doi:10.1029/2003GL017642, 2003.
- Schnitzler, J.-P., Lehning, A., and Steinbrecher R.: Seasonal pattern of isoprene synthase activity in *Quercus robur* leaves and its significance for modeling isoprene emission rates, *Bot. Acta*, 100, 240–243, 1997.
- Sharkey, T. D., and Loreto, F.: Water stress, temperature and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves, *Oecologia*, 95, 328–333, 1993.
- Sharkey, T., Singaas, E. L., Lerdau, M., and Geron, C. D.: Weather effects on isoprene emission capacity and applications in emissions algorithms, *Ecolog. Applications*, 9, 1132–1137, 1999.
- Simon, E., Kuhn, U., Rottenberger, S., Meixner, F. X., and Kesselmeier, J.: Coupling isoprene and monoterpene emissions from Amazonian tree species with physiological and environmental parameters using a neural network approach, *Plant Cell Env.*, 28, 287–301, 2005.
- Simon, V., Dutaur, L., Brouard-Darmais, S., Riba, M. L., and Torres, L.: Biogenic emission by oak trees common to Mediterranean ecosystems, *Environmental monitoring and assessment*,

- 52, 131–139, 1998.
- Simpson, D.: Biogenic emissions in Europe 2. Implications for ozone control strategies, *J. Geophys. Res.*, 100, 22 891–22 906, 1995.
- Simpson, D., Winiwater, W., Borjesson, G., Cinderby, S., Ferreiro, A., Guenther, A. B., Hewitt, C. N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, R., Steinbrecher, R., Svennson, B. H., Tarrason, L., and Oquist, M. G.: Inventorying emissions from nature in Europe, *J. Geophys. Res.*, 104, 8113–8152, 1999.
- Steinbrecher, R., Hauff, K., Rabong, R., and Steinbrecher, R.: Isoprenoid emission of oak species typical for the Mediterranean area: source strength and controlling variables, *Atmos. Environ.*, 31 SI, 79–88, 1997.
- Steinbrecher, R., Klauer, M., Hauff, K., Stockwell, W. R., Jaesche, W., Dietrich, T., and Herbert, F.: Biogenic and anthropogenic fluxes of non-methane hydrocarbons over an urban-impacted forest, Franckfurter Stadtwald, Germany, *Atmos. Environ.*, 34, 3779–3788, 2000.
- Tingey, D. T., Manning, M., Grothaus, L. C., and Burns, W. F.: The influence of light and temperature on isoprene emissions from live oak, *Physiol. Plant.*, 47, 112–118, 1979.
- White, H.: *Artificial Neural Network*, Blackwell, New York, 1992.
- Wiberley, A. E., Linksey, A. R., Falbiel, T. G., and Sharkey, T. D.: Development of the capacity for isoprene emission in kudzu, *Plant, Cell Environ.*, 28, 898–905, 2005.
- Xiaoshan, Z., Yujing, M., Wenshi, S., and Yahui, Z.: Seasonal variations of isoprene emissions from deciduous trees, *Atmos. Environ.*, 34, 3027–3032, 2000.
- Zimmer, W., Brüggeman, N., Emeis, S., Giersch, C., Lehning, A., Steinbrecher, R., and Schnitzler, J.-P.: Process-based modeling of isoprene emission by oak leaves, *Plant Cell Env.*, 23, 585–595, 2000.